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IN-SITU MEASUREMENT OF AOX BIODEGRADATION

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ABSTRACT

The use of chlorine containing compounds in pulp bleaching inevitably leads to the formation of chlorinated organic compounds (AOX). With recently proposed EPA guidelines as to the amount of these compounds that can be released in mill effluent streams, concern has arisen over reducing AOX emissions. One way of accomplishing this is by increasing AOX removal in the secondary treatment system. A technique has been developed to map the degradation of AOX compounds in specific locations throughout the secondary treatment system. The relationship between location and degradation can be used to better understand exactly what is occurring in the treatment system and to determine the most effective modifications to increase treatment efficiency. The technique can also be used as a monitoring tool to determine how these changes affect AOX degradation.

INTRODUCTION

Paper mills have employed biological treatment facilities, such as aerated stabilization basins and activated sludge processes, for the reduction of BOD for many years. Although designed for BOD reduction, these systems do achieve a significant AOX reduction of 30-50% (Bryant *et al.* 1988). Newly proposed regulations for AOX, BOD, and COD levels in effluent streams have caused concern over whether the new limits can be met with current treatment systems.

The mechanism of removal of AOX compounds by biological treatment systems is poorly understood. Mechanisms proposed for AOX removal by aerated lagoon systems include: volatilization, precipitation and settling, sorption onto settling biomass, and chemical and biological degradation (Amy *et al.*, 1988; Bryant *et al.*, 1988). The objective of this study is to measure the biological degradation of AOX in an operating ASB as a function of depth and location. The relationship between depth and location in the basin and biodegradation can be used to determine the conditions that facilitate biodegradation. In-situ measurements of AOX degradation were accomplished by using radiolabeled (^{36}Cl) bleaching filtrates generated in the laboratory. Field results are from Georgia-Pacific's Brunswick mill.

EXPERIMENTAL METHODS

Materials

Chlorine-36 labeled bleaching solutions (Cl_2 and ClO_2) were prepared in the laboratory by the following methods:

Chlorine Dioxide

Radioactive ^{36}Cl had to be converted from $H^{36}Cl$ to an oxidized form in order to make $^{36}ClO_2$. This was accomplished by transferring $^{36}Cl^-$ from $H^{36}Cl$ to chlorate by the equilibrium:

$$3ClO^- \leftrightarrow 2^{36}Cl^- + ClO_3^-$$

The labeled chlorate was recovered by precipitation with potassium chloride.

$$KCl + {}^{36}ClO_3^- \rightarrow K^{36}ClO_3 + Cl^-$$

Chlorine dioxide was then prepared from the labeled chlorate by the Bray method (Bray, 1906).

$$2K^{36}ClO_3 + 2(COOH)_2 \rightarrow 2^{36}ClO_2 + 2CO_2 + (COOK)_2 + 2H_2O$$

Chlorine

Approximately 100 μCi of $H^{36}Cl$ was added to 200 mL of a 2 g/L chlorine water solution. The $^{36}Cl^-$ exchanged with Cl_2 in solution to produce $^{36}Cl_2$ through the equilibrium:

$$H^+ + {}^{36}Cl^- + HOCl \leftrightarrow Cl_2 + H_2O$$

Pulp was bleached with the labeled bleaching solutions to produce ^{36}Cl labeled AOX. Softwood pulp with a kappa number of 33 was bleached at a Cl_2-multiple of 0.21 for Cl_2, and 0.25 for ClO_2. Caustic extraction was conducted at a NaOH level of 0.5×TAC. At the end of each stage, the pulp was filtered through a Buchner funnel with the filtrate being recycled once through the pulp mat. Sodium thiosulfate was added to the C (or D)-stage filtrates prior to storage at 5°C. The E-stage filtrate was adjusted to a pH of 2 with dilute nitric acid prior to storage at 5°C. The C (or D)- and E-stage filtrates from each bleach were mixed then freeze-dried to 10% of their initial volume. Concentrated filtrates were stored in an amber jar at 5°C until used.

Sample cells for the field analysis were constructed by cutting the bottoms out of two 20 mL vials and fusing them

together. This created a cell that could be capped on each end with a membrane. In this study, 0.01 μm track-etched polycarbonate membranes supplied by Poretics were used. These membranes allowed for rapid passage of oxygen and nutrients from the pond while limiting the movement of AOX.

A multiple position sample probe was constructed to allow biodegradation samples to be placed at various depths in the ASB. The probes were constructed from SCH 80 PVC pipe by drilling one inch holes through the pipe at 1 foot intervals. Nylon screws were used to hold the cells in place. Probe sections were constructed in five foot lengths with a union at each end. This allowed for easy transport of the probes and adjustment of the probe length to meet the depth requirements of the ASB. Steel anchor plates were attached to the bottom section to keep the probes submerged.

Methods

For the field study, samples were withdrawn from the ASB at one foot intervals across the depth of the basin. This material was placed in sample cells capped at one end with a 0.01 μm membrane. A 2 mL spike of the concentrated labeled filtrate was added to the sample cells and the cells capped with another membrane. The sample cells were then placed into probes and submerged in the ASB at positions corresponding to the location from which the ASB samples were taken. Four probes were placed near aeration devices (75 hp surface aerators) and 2 probes were placed in a non-aerated area. Probes were deployed in pairs with one probe containing chlorine bleach filtrate samples and the other containing chlorine dioxide bleach filtrate samples. After 5 days, the probes were removed and the sample cell contents transferred to 30 mL vials containing formalin.

Samples were analyzed for both total activity recovered and chloride activity recovered. AOX activity recovered was taken as the difference between the total activity recovered and the chloride activity recovered. Total activity was measured by adding 1 mL of recovered sample to 15 mL scintillation cocktail and counting in a Beckman LS 3801 liquid scintillation counter. To determine the level of activity in the samples attributable to chloride, a modification of the shake flask AOX method was used. A 5 mL aliquot of recovered sample was added to 10 mL water and 2 mL nitrate solution (20g KNO_3 and 1.4 mL HNO_3 diluted to 1 L) in a 125 mL flask. Two 2 mL aliquots were withdrawn and counted. Granular activated carbon (150 mg) was added, the sample was shaken for two hours and then filtered through a 0.45 μm filter. The filter was rinsed with 2 mL nitrate solution and the filtrate counted. To determine the variability of the method, nine samples of $^{36}Cl^-$ in water were analyzed for chloride recovery. An average recovery of 103.1% with a standard deviation of 1% was obtained.

Theory

The membranes used allow for some loss of AOX material by diffusion. Therefore, it was necessary to have an accurate measure of the diffusional AOX loss from the cells in order to determine the difference between AOX loss by diffusion and AOX loss due to biodegradation. Every other sample in each probe was designated as a control sample and the bacterial population in the ASB sample killed prior to addition to these cells. This allowed for the determination of non-biological AOX loss in alternate positions.

Since each cell was in a slightly different environment, diffusion rates had to be normalized in order to compare AOX loss for the various cells. Radioactive chloride ($^{36}Cl^-$), present in the concentrated bleach filtrates as a bleaching byproduct, provided a means to do this. Since the inorganic chloride cannot biodegrade, its loss from the cell must be entirely through diffusion. The rate of inorganic chloride loss was used to account for differences in diffusion rate from one probe position to another.

By assuming that diffusion for both the AOX and inorganic chloride species across the membrane was first order, rate equations could be derived. Comparisons between cells were made by dividing the rate equation for AOX loss by the rate equation for inorganic chloride loss. The rate equation ratios should remain relatively constant for the control samples in each probe if the first order assumption is correct. Biodegradation of AOX in the samples containing live microorganisms will cause the rate ratio for these samples to increase above the control levels.

RESULTS

The results from the first sampling at the Georgia-Pacific mill site in Brunswick, Georgia are presented in Figures 1-6. Figures 1-4 give the ratio of the rate of AOX loss to the rate of chloride loss as a function of depth. Depths which do not have a rate ratio value are representative of positions where a sample cell failure was encountered. As predicted, rate ratios for the control samples for each probe were relatively consistent over the depth of the basin.

Rate ratio information was used to calculate the percent AOX removal in the live samples above that in the control samples (Figs. 5-6).With the exception of the chlorine dioxide samples in the aerated zone, the rate ratios are consistently higher for the live samples than for the control samples. This consistency demonstrates a definite ability of the live bacteria to facilitate the removal of AOX from the

sample cells. At the solids level in the locations sampled (~ 100 mg/L) the sorption of AOX to biomass has been shown to be minimal (Yan and Allen, 1994).

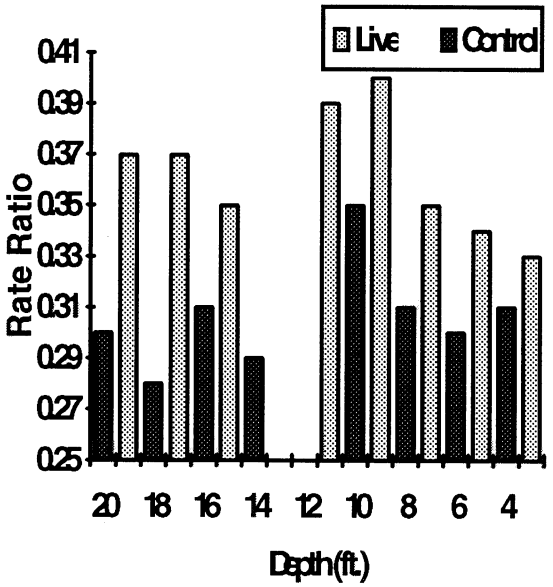

Figure 1. Rate Ratio Vs Depth for Chlorine Samples in the Non-aerated Zone.

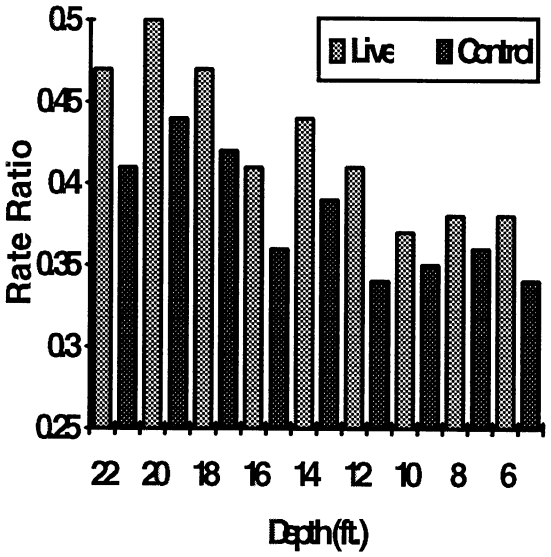

Figure 2. Rate Ratio Vs Depth for Chlorine Dioxide Samples in the Non-aerated Zone.

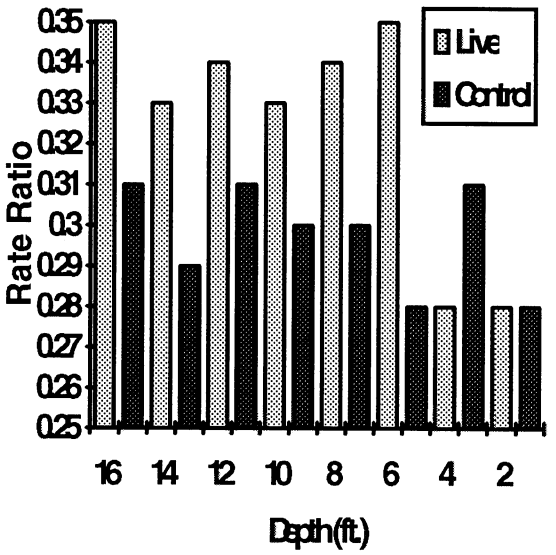

Figure 3. Rate Ratio Vs Depth for Chlorine Samples in the Aerated Zone.

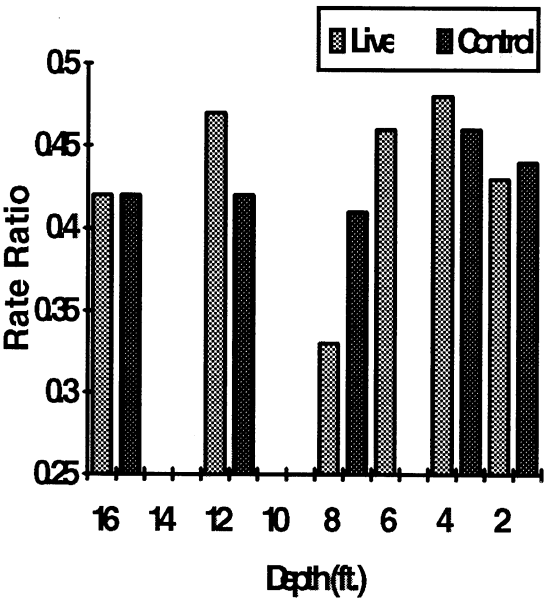

Figure 4. Rate Ratio Vs Depth for Chlorine Dioxide Samples in the Aerated Zone.

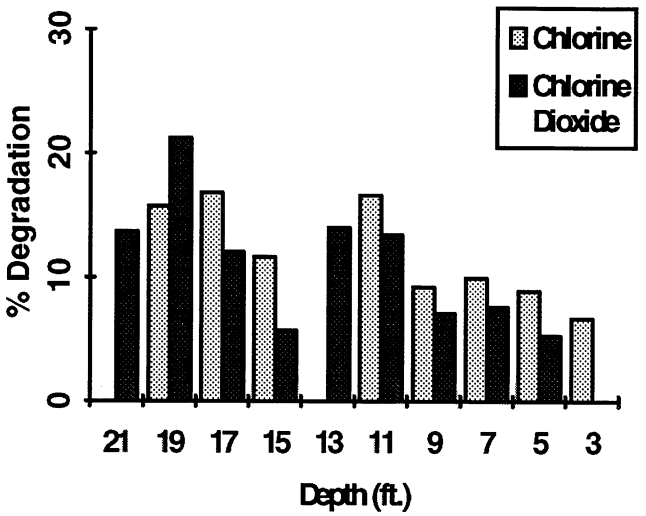

Figure 5. Percent Degradation Vs Depth for the Non-aerated Zone.

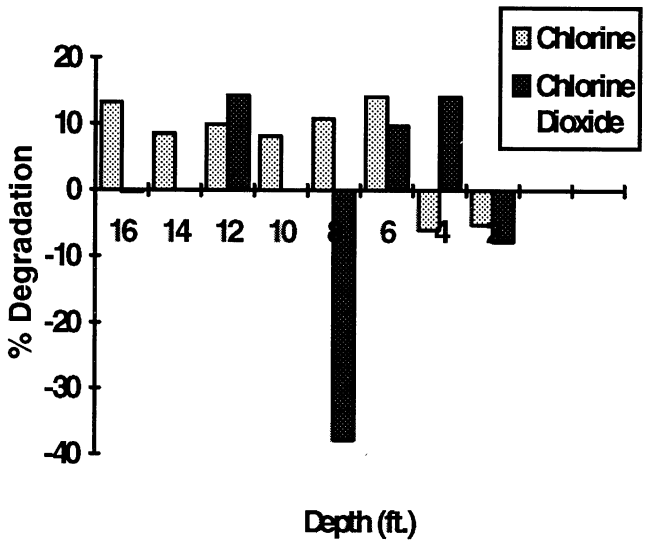

Figure 6. Percent Degradation Vs Depth for the Aerated Zone.

The chlorine bleach filtrate was degraded slightly more than the chlorine dioxide filtrate in both non-aerated and aerated zones. Degradation for the chlorine filtrate was higher in the non-aerated zone than in the aerated zone. Degradation appears to be much more substantial for chlorine dioxide bleach filtrates in the non-aerated zone as opposed to the aerated zones. Statistically, no degradation occurred with the chlorine dioxide bleach filtrate in the aerated zone.

For the non-aerated zone, degradation appears to be higher at the lower depths. This trend is seen for both the chlorine and chlorine dioxide filtrates. No such depth dependence is seen in the aerated zone.

To insure that the control sample cells contained only dead microorganisms and the live cells maintained a viable population, two samples representative of both chlorine and chlorine dioxide filtrates were analyzed. These samples were plated on potato dextrose auger and incubated. After 24 hours, both live samples showed good growth with no growth evident in the control samples. After three weeks, there was still no evidence of growth in the samples streaked with material from the control sample cells.

CONCLUSIONS

- The non-aerated region appears to show a higher level of degradation than the aerated region for both chlorine and chlorine dioxide bleaching filtrates.
- The chlorine bleaching filtrate shows a slightly higher rate of degradation in both the aerated and non-aerated regions than the chlorine dioxide bleaching filtrate.
- The non-aerated region displays a weak depth dependence with degradation being greater at the bottom.
- The 10% degradation observed here is significantly lower than the overall AOX loss reported by the mill. This suggests that mechanism other than biodegradation play major roles in AOX loss from ASB's.

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Portions of this work were used by C.W. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.